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Gregory A. Voth, PI

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Utah
Department of Chemistry
315 S. 1400 E., RM 2020
Salt Lake City, UT 84112-0850

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14. ABSTRACT
The focus of this AFOSR project was the molecular dynamics (MD) simulation of ionic liquid structure, dynamics, and interfacial properties, as well as multi-scale descriptions of these novel liquids (e.g., to bridge with fluid mechanics methods). The overall importance of ionic liquids, as well the challenges for the future in this area, are clearly high priorities for the Air Force advanced propulsion program. During the course of this funding, developed was a highly accurate molecular simulation approach, which included the large effects of electronic polarizability on ionic liquid structure and dynamics. A coarse-grained MD approach was also developed and applied, leading to significant predictions concerning the fundamental behavior of ionic liquids as a function of their chemical composition.

15. SUBJECT TERMS

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A) Objectives

Objectives of original proposal were met and the results are outlined in this final report.

B) Status of Effort for Duration of Funding

In the funding period, several breakthroughs were made in the theoretical study and modeling and simulation of ionic liquids (ILs). A polarizable model was developed to simulate ILs more accurately at the atomistic level. A multiscale coarse-graining methodology was applied to IL systems, extending computer simulations of ILs from microscopic to mesoscopic scales. With these advanced simulation methods, a spatial heterogeneity due to tail aggregation was discovered. The suggested mechanism explains the experimental results, and changed the way people think of IL systems. Based on the tail aggregation phenomenon, the surface layering of IL surface, the micelle formation in IL/water mixture, and the aggregation of hydrophobic molecules in IL systems were observed and systematically explained. They have great values in guiding the real applications of ILs in various conditions. With the above general understanding of IL systems, the physical properties of an IL candidate for propellant, 1-hydroxyethyl-4-amino-1, 2, 4-triazolium nitrate (HEATN), were studied with the all-atom polarizable model. The mechanism suggested for HEATN has provided deep theoretical insight for this specific IL, and will guide more efficient storage and usage of HEATN as propellant.

C) Significant Work Accomplished

1) Atomistic Polarizable Model Development

Room temperature molten salts (RTMS), or ionic liquids (ILs), stimulated a significant body of research. Like inorganic molten salts, ILs are composed solely of ions, but in contrast their melting point is often less than 100 C.[1] Despite the level of research activity, many of the properties of these interesting liquids remained elucidated.[2] This new class of liquid promoted more and more experimental and computational studies. A rich level of detail on the structural and dynamical properties was explored.

For an IL, it was found both in simulation[3-6] and experiment,[7,8] that the local environment around the IL ions was highly anisotropic. For such a system, the particles were not well described as rigid bodies, because their electron densities were distorted during the interactions with each other and the changes in internal structure were basically a many-body effects,[9] which made it highly desirable to model those interactions using a fully polarizable forcefield.[10] Given the high polarizability of IL ions,[11,12] it was a key priority to implement a polarizable model in the computer simulation of IL systems.

Importantly, with this AFOSR-supported project, a polarizable forcefield for the ionic liquids such as 1-ethyl-3-methylimidazolium nitrate ($EMIM^+/NO_3^-$) was developed.[12] The polarizable model was developed based on Thole's smearing dipole model,[13] in which each atomic site was treated as a polarizability center and the anisotropic molecular polarizability could be reproduced through the interaction among the atomic sites.[13,14] Though the polarizable forcefield was initially developed for the IL system $EMIM^+/NO_3^-$, the method is quite general and readily applied on other ILs, such as the 1-hydroxyethyl-4-amino-1, 2, 4-triazolium nitrate (HEATN).

2) Polarizable Molecular Dynamics Code Development

In conjunction with the polarizable IL model mentioned above, a molecular dynamics (MD) Fortran code was also developed and implemented in the DL_POLY MD simulation

package.[15] The long-range multipole interactions (charge-charge, charge-dipole, and dipole-dipole) of the above polarizable forcefield of an infinite system were handled with the Ewald summation method.[16,17] This MD code for the polarizable forcefield was also reasonably well-parallelized with the replicated data method.[18]

In the MD simulations with the polarizable forcefield, the induced dipole could be calculated iteratively,[17,19] or propagated by the extended Lagrangian (ext-L) method.[20] Both methods for the induced dipole were implemented in the MD referenced here. For the iteration method, the induced dipoles are solved iteratively and generally converged in 5 – 6 cycles with a convergence criterion 10^{-5} Debye. For a system size of ~10,000 atoms, the iteration method was very time consuming, even when run on multiple processors. With the ext-L method, however, the induced dipole degrees of freedom were propagated in time, with a proper chosen fictitious mass for each dipole, instead of calculating them iteratively. Therefore, just one cycle was needed for the ext-L method.

The first study for a 400 K bulk simulation[12] for $EMIM^+/NO_3^-$ showed that the main effect of the electronic polarizability would make the ions considerably more mobile when compared to a non-polarizable model, in which the electronic polarizability was not explicitly represented in the forcefield. This effect resulted in a much lower viscosity and significantly higher diffusion constant. Fig. 1 shows the mean square displacement (MSD), on a log-log plot up to 1 ns, of $EMIM^+$ and NO_3^- for both the polarizable and the non-polarizable models. Remarkably, the slope of the MSD of the polarizable model was more than three times larger than the non-polarizable model at the end of 1 ns. The short time inertial motion due to ballistic collisions lasts less than 0.1 ps, followed by a long time intermediate region (~100 ps for the polarizable model and ~800 ps for the non-polarizable model), finally limited to linear diffusion. A linear fit to the MSD between 900 – 1000 ps and use of the Einstein relation, $<\Delta r(t)^2>=6Dt$, gave self-diffusion constants of 1.49×10^{-10} m^2/s and 1.55×10^{-10} m^2/s for polarizable $EMIM^+$ and NO_3^-, respectively, and 5.07×10^{-11} m^2/s and 4.80×10^{-11} m^2/s for non-polarizable $EMIM^+$ and NO_3^-, respectively.

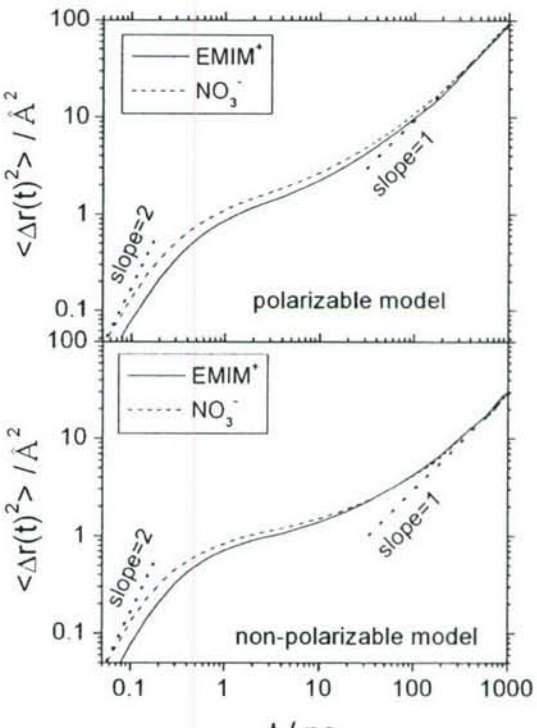

Figure 1 Mean square displacements of EMIM+ and NO3- for both the polarizable and non-polarizable models.

3) Multiscale Coarse-Graining Model Development

A multi-scale coarse-graining (MS-CG) approach[21] was applied to the $EMIM^+/NO_3^-$ IL to construct a MS-CG model for ILs. The short-range non-bonded forces between CG sites were force-matched by an extended least-square force-matching method, while the bonded forces between intramolecular CG sites were retrieved from the configurational data from the polarizable atomistic MD simulations. This MS-CG model rebuilt satisfactory structural and thermodynamic properties and showed significant time integration efficiency (factors of

hundreds speed-up). Simulations of large IL systems, for long periods of time, are therefore possible with this MS-CG model.

4) Spatial Heterogeneity and Domain Diffusion in Ionic Liquids

By extending the MS-CG model, a spatial heterogeneity due to cationic tail aggregation has been discovered.[22] It has been found that, with sufficiently long side chains, the tail groups of cations aggregate to form spatially heterogeneous domains (white spheres in Fig. 2). This is understood as the result of competition between the charged electrostatic interactions between head groups and anions and the collective short-range interactions between the neutral tail groups. This aggregation helps to explain a number of experimentally[23,24] observed physical phenomena in ILs, especially the mesoscopic liquid crystal-like inhomogeneity, which exists in IL systems.[25-28]

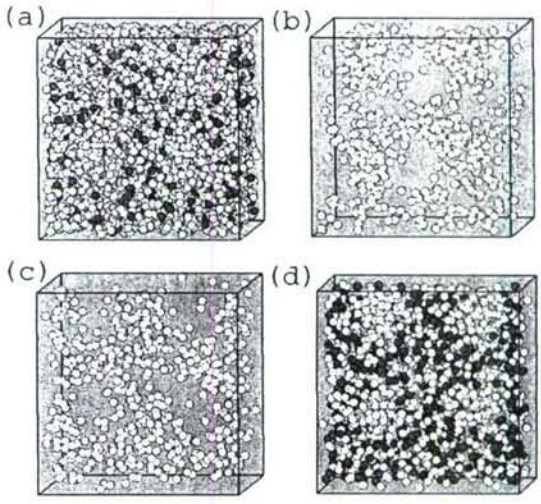

Figure 2 Spatial heterogeneity due to tail aggregation in ionic liquids. (a) All CG sites. (b) Tail groups only. (c) Head groups only. (d) Head groups, tail groups, and anions.

The extended MS-CG model was then used to qualitatively investigate the phase transition of tail domains.[29] It was found that, with a sufficiently long alkyl chain at a low enough temperature, the tail domains remain relatively stable, despite the diffusion of individual ions in the liquid phase; With increasing temperature, the average tail domains began to diffuse, while beyond a transition temperature, their average density had an almost uniform distribution, although the tail groups continued to form instantaneous domains. Fig. 3 shows the average tail density of the $BMIM^+/NO_3^-$ system with 64 ion pairs calculated by the newly defined heterogeneity order parameter.[29,30] Each sphere represents the ensemble-averaged local density in that location. The warmer the color, the higher the tail density. It can be seen that, below the transition temperature T_c = 1200 K, the tail domains have relative stationary positions; while above T_c, they move around so that on average they distribute almost uniformly.

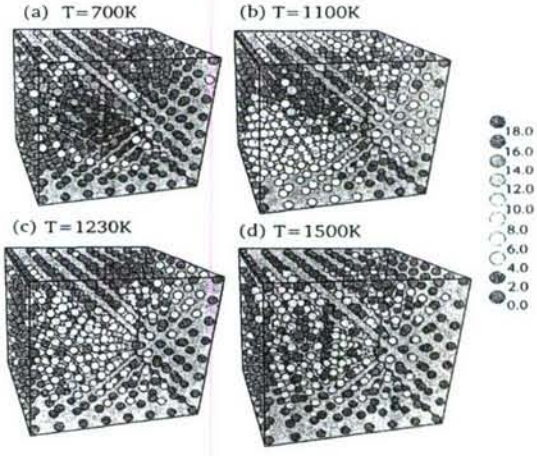

Figure 3 Tail domain diffusion in ionic liquids.

The atomistic polarizable model was extended to the $XMIM^+/NO_3^-$ ILs with the carbon groups on their cationic side chains ranging from 2 to 12.[30] These polarizable atomistic models were used to refine the spatial heterogeneity discovered earlier[22] by the MS-CG model. While the tail groups were still found to aggregate (white spheres in Fig. 2), the more detailed atomistic models discovered the continuous polar network composed of the charged cationic head groups and the anions (yellow and red spheres in Fig. 2), as reported earlier by Lopes and

Pádua.[31] We have interpreted the formation of the continuous polar network as the following. Due to their strong electrostatic interactions, the anions always stay close to the head groups. The charged groups retain their local structures relatively unchanged, forming a continuous polar network, and leading to different global structures when varying the side-chain length. The atomistic simulation results are quantitatively comparable to experimental results. The tail aggregation mechanism we have suggested based on the simulation results explains very well the experimentally[21,30,32] observed increasing viscosity and decreasing mass density with increasing side-chain length.

5) Roughness and Layering of Ionic Liquid Surface

The IL/vacuum interface has been investigated with both the atomistic[33] and the MS-CG[34] models. The $EMIM^+/NO_3^-$ IL was first simulated by both the non-polarizable and the polarizable atomistic models at T = 400 K. The cations and the anions were found to have an enhanced density on the interface. By using the second Legendre polynomial, it was clearly shown that the cations on the interface tend to be perpendicular to the surface with their ethyl tail groups protruding outward. One snapshot of the IL surface is given in Fig. 4. Balls and sticks represent the atoms on the surface, while lines represent the underlying ones. This picture clearly shows the roughness of the IL surface. This study also demonstrated that the polarization effect is important for the IL surface. In particular, the surface tension given by the polarizable model was much smaller than that given by the non-polarizable model and closer to that of the experimental.

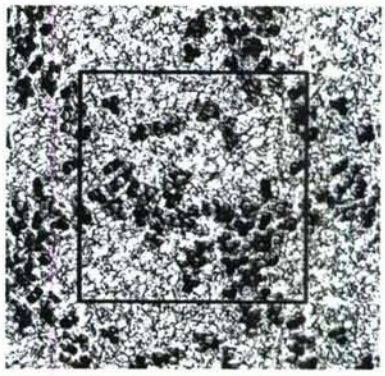

Figure 4 One snapshot of the ionic liquid surface.

The simulation results by the MS-CG model[34] for $EMIM^+/NO_3^-$ also showed the same surface behavior of cations. In order to study the effect of the alkyl side-chain length to the surface behavior, the side chain of the MS-CG model for the EMIM+/NO3- IL was elongated to build the CG models for XMIM+/NO3-, with the carbon groups on their cationic side chains ranging from 4 to 12, which were then used to perform the surface MD simulations for the longer-chain systems. The surface tension decreased, while the side-chain length increased. A multilayer ordering appeared more clearly for longer cationic side-chain systems (shown in Fig. 5). Detailed analysis indicated that such multilayer ordering is also resulted from the strong short-range interaction of the tail groups. Thus, the behavior of the IL surfaces were governed by the tail aggregation mechanism in a two dimensional regime. This mechanism better explains the experimental results[35-39] than does the mechanisms[37,38] suggested by others. Expected, is the unification of the understanding of the surface behavior of IL systems and further guided experimental

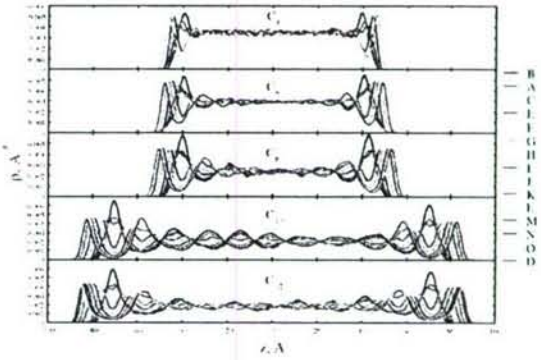

Figure 5 Density profiles of different CG sites along the normal direction of IL surface.

and theoretical investigations of IL interfaces.

6) Micelle Formation in Ionic Liquid/Water Mixture

MD simulations[40] with the non-polarizable atomistic force field were carried out to investigate the influence of water on the spatial heterogeneous distribution of ionic liquids. It was found that, by increasing the amount of water, the spatial heterogeneity of the ionic liquid first increases, and then stays on its maximum in a narrow range of water concentration, before it decreases drastically. Fig. 6 shows one snapshot for the IL/water mixture with a water molar fraction of 0.75, when the IL exhibits the strongest aggregation. The cationic tail groups (yellow spheres) aggregate to form relatively isolated tail domains, bordered by the continuous polar network composed of the cationic head groups (red spheres) and the anions (pink spheres), while the water molecules (blue spheres) are embedded in the polar network. In contrast, the ionic diffusion monotonically grows with the aqueous concentration. These phenomena are understood as the result of the continuous competition between the enhanced hydrophobic interaction of the cationic tail groups and the attenuation of the ion-ion interactions with increasing amount of water. This mechanism successfully explains the experimentally[41,42] observed micelle formation of ionic liquids in aqueous solutions and agrees with the general surfactant critical micelle concentration theory.[43]

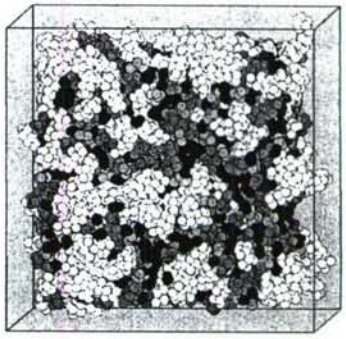

Figure 6 Micelle Formation in IL/water mixture.

7) Aggregation of Hydrophobic Molecules in Ionic Liquids

Continued MD simulations were carried out to investigate the aggregation of small non-polar particles in ionic liquids.[44] Fig. 7 shows the aggregation of methane molecules in $BMIM^+/CL^-$. The aggregation of non-polar molecules decreases with increasing symmetries of the anions, or equivalently, decreases with decreasing strength of electrostatic attraction between polar head/anion groups. For a given anion, the aggregation decreases with increasing length of the side chain. A comparison between methane and butane shows that methane molecules have much stronger aggregation tendency than butane. The above results can be explained by a unified entropic origin within the framework of the previous revealed spatial heterogeneity phenomenon due to tail aggregation[22,29,30].

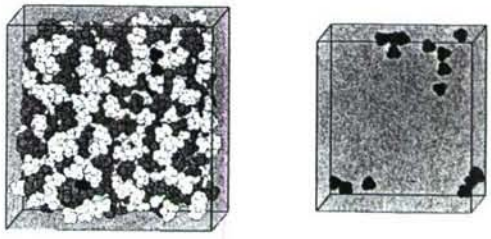

Figure 7 Aggregation of hydrophobic molecules in ionic liquids.

8) Physical Properties of HEATN

An atomistic polarizable model was developed for 1-hydroxyethyl-4-amino-1, 2, 4-triazolium nitrate (HEATN), an energetic IL, which is a good candidate for ionic fuel and propellant, and used in the MD simulations to investigate its physical properties. The upper panels in Fig. 8 show the mean square displacements of ions with different time scales at various temperatures. The two lower panels in Fig. 8 show the self-diffusion coefficients vs. temperature. A glass transition point at T = 275 K was unambiguously identified. A complex hydrogen bond network was revealed in HEATN, which is responsible for the poor packing efficiency of ions and the low melting/glass transition point of HEATN. The densities calculated from the simulation data are 1.436 g/cm^3 and 1.427 g/cm^3, respectively, for the polarizable and non-polarizable models. The viscosities were fitted as 64.25 and 38.21 c.p., for the non-polarizable and polarizable models, respectively. Essentially, both the high viscosity and poor ion packing of HEATN can be attributed to the introduction of hydroxyl and amino groups in its molecular structure.

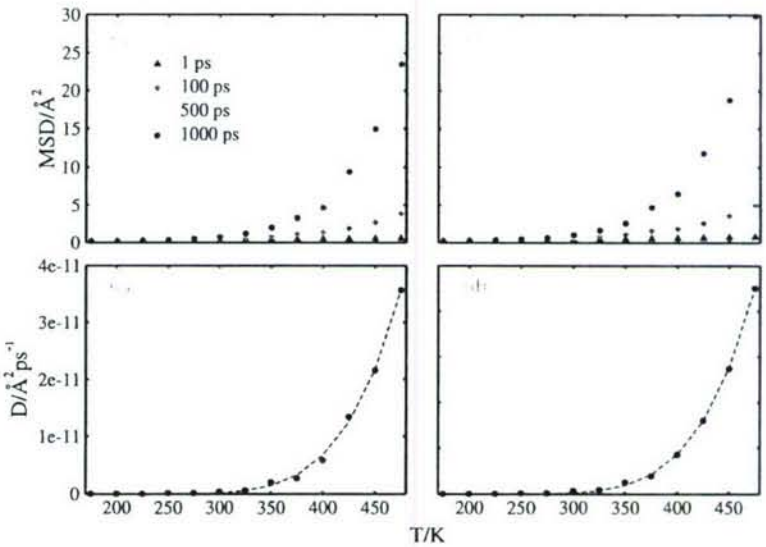

Figure 8 Mean square displacements and diffusion constants of HEATN at different temperatures.

9) Extendable Multiscale Coarse-Graining Models Development

The efficient use of ILs required the technique of systematic design of ILs. The analysis of the interactions between building blocks was essential for the development of this technique. The MS-CG methods developed can obtain the effective forces between CG sites (building blocks).

An effective force coarse-graining (EFCG) method[45] was developed as a complement to the general MS-CG method and applied to the EMIM$^+$/NO$_3^-$ IL. By compromising some accuracy of the local structures, the EFCG force fields were transferable between different thermodynamic conditions. The EFCG force field for EMIM$^+$/NO$_3^-$ was found to be applicable when generating the force fields for similar ILs with

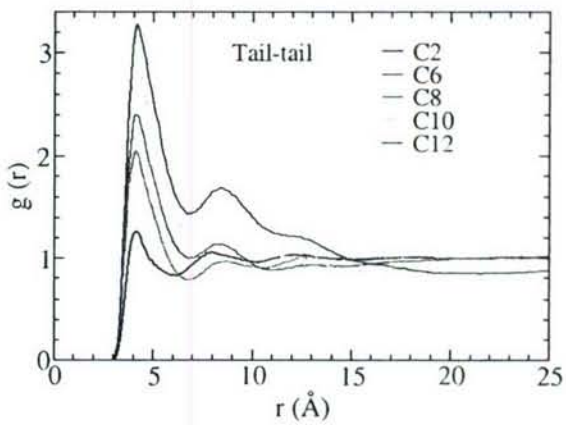

Figure 9 Radial Distribution Functions between tail groups for the IL systems with different alkyl side-chain lengths.

longer alkyl side chains by rescaling the effective electrostatic forces according to the partial charges on the CG sites.[46] Fig. 9 demonstrates the radial distribution functions between the cationic tail groups obtained from the CG MD ran with the extended EFCG force fields for the ILs with different alkyl side-chain lengths. The numbers represent the number of carbon groups on the side chain. Fig. 9 clearly shows that when increasing alkyl side-chain length, the aggregation of the cationic tail groups became stronger, and this tendency agreed with that observed in previous all-atom MD simulations.[30] Because the EFCG force fields were extendable for longer side-chain IL systems and transferable between different thermodynamic conditions, they were especially suitable for constructing the effective force library of IL building blocks. Choosing building blocks of ILs according to the features of their effective forces allowed systematic design of ILs to meet customized application requirements.

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(42) Seddon, K. R.; Stark, A.; Torres, M.-J. Influence of Chloride, Water, and Organic Solvents on the Physical Properties of Ionic Liquids. *Pure Appl. Chem.* **2000**, *72*, 2275.
(43) Nagarajan, R.; Wang, C.-C. Solution Behavior of Surfactants in Ethylene Glycol: Probing the Existence of a Cmc and of Micellar Aggregates. *J. Colloid Interface Sci.* **1996**, *178*, 471.
(44) Jiang, W.; Voth, G. A. Aggregation of Small Non-Polar Particles in Ionic Liquids. *J. Phys. Chem. B* **2007**, *To be submitted.*
(45) Wang, Y.; Noid, W. G.; Liu, P.; Voth, G. A. Effective Force Coarse-Graining. *J. Phys. Chem. B* **2007**, *To be submitted.*
(46) Wang, Y.; Feng, S.; Voth, G. A. Extendable Coarse-Grained Model for Ionic Liquids. *J. Phys. Chem. B* **2007**, *To be submitted.*

C. Executive Summary:

1) Production of Thesis Dissertations

None

2) Significant Advances and Conclusions

The focus of this AFOSR project was the molecular dynamics (MD) simulation of ionic liquid (IL) structure, dynamics, and interfacial properties, as well as multiscale descriptions of these novel liquids (e.g., bridging with fluid mechanics methods). The overall importance of ionic liquids, as well the challenges for the future in this area, were at the time of this proposal and continue to be, clearly, high priorities for the Air Force advanced propulsion program. During the course of award period, MD simulations were employed to study the physical properties of an energetic ionic liquid, 1-hydroxyethyl-4-amino-1, 2, 4-triazolium nitrate (HEATN). The aggregation of small non-polar molecules have been observed to strongly aggregate in the ILs, and the strength of aggregation varies for different cation/anion combinations. A transferable and extendable multiscale coarse-graining (MS-CG) model was developed for the ILs, which enabled the systematic design of ILs at the CG level. When combining accomplishments, which

includes developing an all-atom polarizable model for ILs, developing the MS-CG models for ILs, discovering the spatial heterogeneity in ILs due to tail aggregation and the tail domain diffusion phenomena, revealing the surface layering phenomenon on the IL surface, and investigating the influence of water concentration on the tail aggregation, the research efforts lead to significant new predictions concerning the fundamental behavior of ILs as a function of their chemical composition and open the door towards systematic design of ILs to meet customized application requirements.

3) Collaborations (inclusive of those formed and the publications emerging from)

None

4) Research Effort of Supported and Involved Personnel

Personnel Supported	Title/Description	Effective Dates	% Effort
Dr. Gregory A. Voth	Distinguished Prof. & Lead PI	06/2004 & 06/2005	20% total
Dr. Gary Ayton	Assistant Research Professor	07/2006 – 12/2006	65%
Dr. Christian Burnham	Postdoctoral Research Fellow	08/2004 – 11/2004	100%
Dr. Yeshitila Gebremichael	Postdoctoral Research Fellow	07/2004 – 10/2004	100%
Dr. Yanting Wang	Postdoctoral Research Fellow	09/2004 – 12/2006	100%
Dr. Tianying Yan	Postdoctoral Research Fellow	03/2004 – 07/2004	100%
Wei Jiang	Graduate Student Researcher	05/2005 – 12/2006	100%
Dr. Jian Zhou	Postdoctoral Research Fellow	04/2005 – 06/2005	100%

5) Total Publications Supported

1. Del Pópolo, M. G.; Voth, G. A., On the Structure and Dynamics of Ionic Liquids. *J. Phys. Chem. B* **2004**, 108, 1744.

2. Yan, T.; Burnham, C. J.; Del Pópolo, M. G.; Voth, G. A., Molecular Dynamics Simulation of Ionic Liquids: The Effect of Electronic Polarizability. *J. Phys. Chem. B* **2004**, 108, 11877.

3. Wang, Y.; Voth, G. A., Unique Spatial Heterogeneity in Ionic Liquids. *J. Am. Chem. Soc* **2005**, 127, 12192.

4. Yan, T.; Li, S.; Jiang, W.; Gao, X.; Xiang, B.; Voth, G. A., Structure of the Liquid-Vacuum Interface of Room-Temperature Ionic Liquids: A Molecular Dynamics Study. *J. Phys. Chem. B* **2006,** 110, 1800.

5. Wang, Y.; Izvekov, S.; Yan, T.; Voth, G. A., Multiscale Coarse-Graining of Ionic Liquids. *J. Phys. Chem. B* **2006**, 110, 3564.

6. Wang, Y.; Voth, G. A., Tail Aggregation and Domain Diffusion in Ionic Liquids. *J. Phys. Chem. B* **2006**, 110, 18601.

7. Jiang, W.; Wang, Y.; Yan, T.; Voth, G. A., Molecular Dynamics Simulation of Nanostructural Organization in Ionic Liquid/Water Mixtures. *J. Phys. Chem. B* **2007**, 111, 4812.

8. Wang, Y.; Jiang, W.; Voth, G. A., Spatial Heterogeneity in Ionic Liquids. *ACS Symp. Ser. Book in Ionic Liquids* **2007,** in press.

9. Yan, T.; Wang, Y.; Gao, X.; Voth, G. A., On the Structure of Ionic Liquids: Comparisons between a Polarizable Model and a Non-Polarizable Model I. Structural Properties *J. Phys. Chem. B* **2007,** to be submitted.

10. Yan, T.; Wang, Y.; Gao, X.; Voth, G. A., On the Dynamics of Ionic Liquids: Comparisons between a Polarizable Model and a Non-Polarizable Model II. Dynamical Properties *J. Phys. Chem. B* **2007,** to be submitted.

11. Jiang, W.; Wang, Y.; Yan, T.; Voth, G. A., Simulation of the Liquid/Vacuum Interface of Room-Temperature Ionic Liquids with alkyl substituents of different lengths: A Multi-Scale Coarse-Graining Study *J. Phys. Chem. B* **2007,** to be submitted.

12. Jiang, W.; Yan. T.; Wang, Y.; Voth, G. A., Computer Simulation of Physical Properties of Energetic Room Temperature Ionic Liquid, 1-Hydroxyethyl-4-Amino-1,2,4-Tirazolium Nitrate (HEATN), *J. Phys. Chem. B* **2007,** to be submitted.

13. Jiang, W.; Voth, G. A., Aggregation of Small Non-polar Particles in Ionic Liquids. *J. Phys. Chem. B* **2007,** to be submitted.

6) Interactions/Transitions

(a) Participation:

1. "The Frontier Beyond Molecular Dynamics Simulation: Systematic Multi-Scale Coarse-Graining of Complex Systems," Chemical Engineering Department Seminar, University of Naples, Italy, September, 2004.

2. "A Multi-Scale Coarse Graining Method for Condensed Phase Systems," International Workshop on Theoretical and Computational Chemistry of Complex Systems and 3rd Chinese Theoretical and Computational Chemistry Conference, Hong Kong, January, 2005.

3. "Multi-Scale Simulations of Ionic Liquids," AFOSR Contractor's Meeting, Monterey California, May, 2005.

4. "Systematic Coarse-graining of Condensed Phase Systems," Materials Division Seminar, Air Force Research Laboratory, Wright-Patterson Air Force Base, December. 2005.

5. "Molecular Dynamics and Coarse-grained Simulations of Ionic Liquids," Invited Seminar at the Air Force Office of Scientific Research Workshop on Ionic Liquids, University of Alabama, February, 2006.

6. "Multiscale Simulation of Ionic Liquids: An Emerging Picture of Their Unique Dynamical and Structural Behavior," Invited Seminar in the Symposium on Ionic Liquids: Not Just Solvents Anymore, ACS Division of Industrial and Engineering Chemistry, National American Chemical Society Meeting, Atlanta, Georgia, March 2006.

(b) Consulting/Advisory Functions:

Gaussian, Inc.

(c) Transitions:

The simulation capability developed in this project is available to DoD researchers at Edwards AFB and elsewhere to aid in the design and analysis of new ionic liquids for propulsion purposes.

New Discoveries, Inventions, Patents:

None

Honors/Awards:

John Simon Guggenheim Memorial Fellowship, 2004 – 2005.